“Sprayed Bio-carbonaceous Films and Their Chemiresistive Application”

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Submitted by

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Introduction

Gas sensor is the device used to detect the hazardous and toxic gases present in environment and expelled by the chemical industries and automobile fuel combustion. The rapid industrialization of our society has made it necessary for measurement technologies for monitoring of various gasses, and fumes to grow in parallel. At present, detection of toxic gases became a point of necessity to maintain the environmental balance. The developments of miniature and portable gas sensor that are able to detect these gases in real time with good sensing performance will significantly impact our daily life. In the last few years there has been an explosion in the number of published papers dealing with nanomaterials for gas sensor application. Gas sensor is the device that is of supreme importance. There is a need for simple, sensitive and stable electronic sensors suited for trace detection in a wide spectrum of application ranging from lab-on-chip and in vivo biosensors to environmental monitoring and warfare agent detection, as opposed to the often employed expensive, bulky and complicated instrumental method. Inexpensive and low-power devices are fuelling the exponential growth of research in this area. Researchers are trying to fabricate nanomaterials that would work as better gas sensor with fast response, long-term stability, high sensitivity, and greater selectivity. There is an important point to be concerned to control and monitor these harmful species, considering a huge risk of damage to assets and human beings if a leak occurs. There are certain gases which are toxic to human and environmental lives as they cause big explosion. Accordingly, there is a need of gas sensor with the intention of continuous and effective detection of these gases to evade predominantly the above said dangers.

Motivation

Gas sensor plays crucial role in many important areas such as environmental monitoring, automotive applications, domestic safety, public security, air-conditioning in aero planes, spacecrafts, etc. In 1984 more than 16000 people died, 5,58,125 people injured and 3,900 severely and permanently disabled in Bhopal disaster, also known as Bhopal gas tragedy. It was a gas leak incident in the Union Carbide India Limited (UCIL) pesticide plant. It occurred on the night of 2-3 December 1984 in Bhopal, Madhya Pradesh. In Germany every year approximately 600 people die, 6,000 seriously injure and 60,000 slightly injure in domestic fire accident. Most of them die due to the air pollution i.e. poisoning with smoke during night. The victims are unconscious in sleep and suffocate. Since the late 1970s, Europe's main political concern is air

pollution. In 1996, the European Council adopted a Framework Directive on ambient air-quality assessment and management, Directive - 96/62/EC of September 27, 1996. In an automotive industry, metal oxide gas sensors are used to improve the comfort of a vehicle's occupants. The output of any gas sensor must provide a signal, which corresponds to levels of pollution and smell, which is proportional to the gas concentration. To analyze the air quality sensors based on the change in resistivity of metal oxide semiconductors are primarily used. The metal oxide gas sensors have significant advantages compared to mass sensitive sensors or thermal conductivity sensors. High sensitivity, selectivity and stability, fast response and recovery time, low detection limit for the gas, a low dependence on humidity and temperature, a long service life and relatively low product costs are the advantages of onion mediated carbon sensors. Taking these advantages into consideration, researchers are motivated towards carbon sensors.

An overview of relevant literature

In recent years, carbon-based materials such as carbon nanotubes, graphene and graphene oxide etc., have shown excellent gas sensor properties [1-5]. The natural carbon sources, used for the synthesis of functional carbon materials, and their applications have also been studied by different groups of researchers worldwide. Yuan *et al.* used a facile and green strategy for fabrication of carbon-foam with tunable pore structure by controlling the amount of yeast and water in bread [6]. Rybarczyk *et al.* fabricated a series of carbon materials from natural rice husk and further envisaged in Li−S battery [7]. Carbon-based materials are a potential next generation gas sensor material for autonomous sensor technology, since they have excellent detection sensitivity with interesting energy conversion characteristics [8]. The absence of certain atoms and the reconstruction of the lattice due to annealing lead to most of the intrinsic defects in the carbon nanostructure [9]. The intrinsic defects in carbon nanostructures include point defects (vacancies, Stone–Wales defects) and line defects (dislocation, grain boundaries) and in-plane topological defects (non-hexagonal rings, such as pentagons and heptagons), which undoubtedly break the electron–hole symmetry, alter the local density of the π electrons, increase the chemical reactivity, and modify the edges and induce expected local active sites [10]. Ghule *et al.* fabricated a graphene oxide using microwave assisted carbonization of market quality table top sugar [11]. In previously reported carbon-based sensor studies, it has been shown that single and multiwall carbon nanotubes (SWCNT and MWCNTs) functionalized with nanoparticles (NPs) such as Au, Pd and Ag [12], or (MWCNTs)–polymer composite-based

hybrid gas sensors [13], exhibits improved selectivity toward specific gases, as well as improved electrical response. Abdelhalim *et al.* examined the response of CNT-based gas sensor functionalized with Au, toward different ammonia concentrations, varying from 10 -100 ppm. They found that upon exposure to 100 ppm of the target gas, the sensor reached normalized response of 92 % [13] Similar to CNT-based sensors, graphene and reduced graphene oxide have proven to be promising candidates toward the detection of reducing gases, such as H_2, CO, NH_3, CH_4, NO, etc. However, their fictionalization with metals, and conducting polymers such as polyaniline (PANI), lead to their improved selectivity and greater electrical response, compared to those sensors that were not functionalized. Huang *et al.* studied an ammonia gas sensor based on reduced graphene oxide (RGO)-polyaniline (PANI) hybrids, and showed that while the unmodified RGO based sensor exhibited about 5.2% change in the normalized resistance when exposed to 50 ppm of ammonia. When used for the same ammonia concentration, the hybrid material exhibited an improved response of 59.2 % [12]. Wang and co-workers fabricated an ammonia gas sensor based on chemically reduced graphene oxide with pyrrole vapor, Py-rGO. The response of the sensor was examined at various ammonia concentrations ranging from 5 ppb to 100 ppm, and it was shown that the sensor exhibited about 4.2 % increase in the normalized resistance upon exposure to 5 ppb of the target gas, and about 22 % increase upon exposure to 100 ppm [14].

Experimental research method

There are several methods reported in literature for synthesizing carbon nanostructures which are not limited to synthetic methods such as chemical vapor deposition (CVD), successive ionic layer adsorption and reaction (SILAR), Chemical bath deposition (CBD), spray pyrolysis, microwave-assisted synthesis, and hydrothermal synthesis to name a few. Among these synthesis methods, spray pyrolysis has several advantages such as, cleanliness, inexpensive, and trouble free. Spray pyrolysis has many merits over traditional heating which provides increased reaction kinetics due to its unique operation style. Heating provides enhanced chemical reaction rate, which results in cleaner reaction products with higher yields, and is a productive route to nanostructuring of a range of oxides and bio-carbon/carbon.

In my present work I will synthesis bio-carbonaceous film from onion juice using spray pyrolysis synthesis method. This scalable and cost-effective method forms a carbonaceous product which is nanocrystalline, mesoporous, and exhibits a high surface area. In addition to the

effectiveness in gas sensing applications, in presence of various oxidizing and reducing gases, the structure, morphology, porosity, pore-size distribution etc., has will be studied in detail. The selectivity of a "bio-carbonaceous film" sensor will be determined against various gases like ammonia, acetone, methanol, ethanol, toluene, and commercial gases such as carbon monoxide (CO), carbon dioxide (CO_2), Liquefied Petroleum Gas (LPG), nitrogen dioxide (NO_2), hydrogen sulphide (H_2S), etc.

Finally, the structural and morphological properties of the prepared films will be studied using various characterization techniques mentioned below:

1. X-ray Diffraction (XRD)
2. Field emission scanning electron microscopy (FE-SEM)
3. Energy Dispersive X-Ray Spectroscopy (EDAX)
4. Transmission electron microscopy (TEM)
5. X-ray photoelectron spectroscopy (XPS)
6. The Brunauer–Emmett–Teller (BET)

Sensor measurements

A schematic illustration of the sensor unit with a gas sensing experimental setup is shown in Figure 1. The gas sensor unit consists of a stainless-steel cylindrical chamber with 250 mL volume capacity. The cylindrical chamber consists of heater with PID controller to set the desired temperature. A voltage stabilizer is used to provide constant voltage to avoid the fluctuations in the temperature. The change in resistance of the sensor, due to the presence of target gas, can be recorded by using Computer assisted 6- digit Keithley 6514 System electrometer. Keithley electrometer was coupled to the computer via RS232 interface to record the change in resistance with respect to time. For electrical contacts silver paste, on the sensor film, will be preferred. The target gases used in the experiments will be obtained (Cryo gases Pvt. Ltd, Mumbai, India) in 0.5 L canisters with each of 1000 ppm concentration.

The gas response will be calculated from the following relation;

$$\boldsymbol{S}\% = \frac{\boldsymbol{R_a - R_g}}{\boldsymbol{R_a}} \times \mathbf{100} \quad (1)$$

where, R_a is the stabilized resistance of the sensor material in presence of air, R_g is the stabilized resistance in presence of the target gas. The desired concentration of target gas was obtained by the static liquid gas distribution method, which was calculated by the following formula.

$$\mathbf{C\ ppm} = \frac{\mathbf{22.4\rho TV'}}{\mathbf{273MV}} \times \mathbf{1000} \quad (2)$$

where, C (ppm) is the desired target gas concentration; ρ is (g/mL) the density of the liquid; 'V' is the volume gas (μL), T is testing temperature (K), M is the molecular weight of target gas (g mol^{-1}), and V is the volume of testing chamber (L).

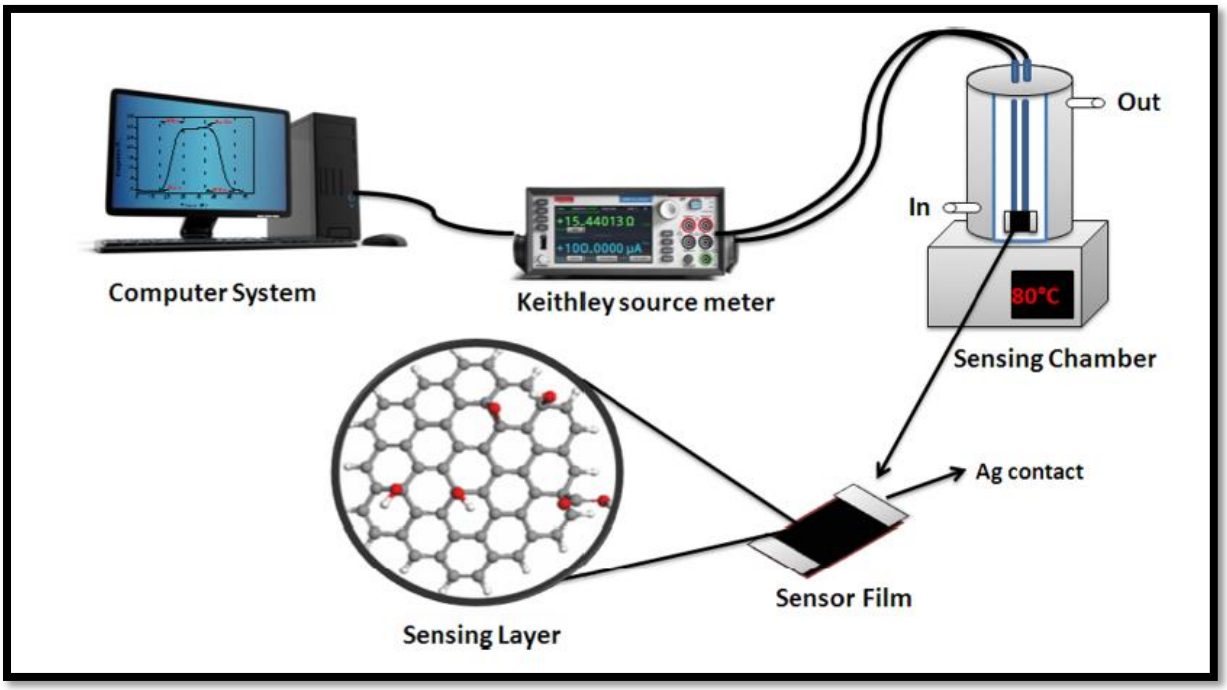

Figure 1: A schematic illustration of the sensor unit with a gas sensing experimental setup.

Objectives

1. To use eco-friendly and cost-effective spray pyrolysis method for synthesis of bio-carbonaceous film from onion Juice.
2. To investigate structural and surface morphological properties of the prepared bio-carbonaceous film using different characterization techniques mentioned earlier.
3. To measure the Chemiresistive properties of these nanomaterials for various gases mentioned earlier.
4. To study the effect of the concentration on the gas sensing properties of the prepared nanomaterials.

5. To study the effect of the doping of the various metals like Zn, Ni, Co, Mn, etc on the gas sensing performance of the bio-carbonaceous.

References

1. Dube, I.; Jime´nez, D.; Fedorov, G.; Boyd, A.; Chenko, I. G.; Paranjape, M. and Barbara, P. Carbon, 2015, 87, 330-337.
2. Rigoni, F.; Drera, G.; Pagliara, S.; Goldoni, A. and Sangaletti, L. Carbon, 2014, 80, 356-363. Page 25 of 33 ACS Paragon Plus Environment ACS Applied Materials & Interfaces
3. Slobodian, P.; Riha, P.; Lengalova, A.; Svoboda, P. and Saha, P. Carbon, 2011, 49, 2499-2507.
4. Cho, W. S.; Moon, S.; Paek, K. K.; Lee, Y. H.; Park, J. H. and Ju, B. K. Actuators B: Chem., 2006, 119, 180- 185.
5. Collins, P. G.; Bradley, K.; Ishigami, M. and Zettl, A. Science, 2000, 287, 1801-1804.
6. Yuan, Y.; Ding, Y.; Wang, C.; Xu, F.; Lin, Z.; Qin, Y.; Li, Y.; Yang, M.; He, X.; Peng, Q. and Li, YACS Appl. Mater. Interfaces, 2016, 8(26), 16852-16861.
7. Rybarczyk, M.K.; Peng, H.J.; Tang, C.; Lieder, M.; Zhang, Q. and Titirici, M.M. Green Chemistry, 2016, 18(19), 5169-5179.
8. Baughman, R. H.; Zakhidov, A. A. and De Heer, W. A. Science, 2002, 297 (5582), 787-792.
9. Neto, A. C.; Guinea, F.; Peres, N. M.; Novoselov, K. S. and Geim, A. K. The electronic properties of graphene, Rev. Mod. Phy., 2009, 81 (1), 109 (1-55).
10. Tangand, C. and Zhang, Q. Adv, Mater., 2017, 1604103 (1-9).
11. B. G. Ghule, S. Shaikh, S. U. Ekar, U. T. Nakate, K. C. Gunturu, N. M. Shinde and R. S. Mane, ACS appl. mater. & interfaces, 2017, 9, 43051.
12. X. Huang, N. Hu, R. Gao, Y. Yu, Y. Wang, Z. Yang, E. Siu-Wai Kong, H. Wei, Y. Zhang, J. Mater. Chem., 2012, 22, 22488.
13. A. Abdelhalim, A. Abdellah, G. Scarp, P. Lugli, Nanotechnol., 2014, 25, 055208.
14. R. Mangu, S. Rajaputra , V. P. Singh, Nanotechnol., 2011, 22, 215502.